

## PATENT SPECIFICATION

NO DRAWINGS

1084070

1084070



Date of Application and filing Complete Specification: June 2, 1966.

No. 24594/66.

Application made in Germany (No. K56297 Vlb/15 I) on June 3, 1965.

(Patent of Addition to No. 950761 dated July 28, 1961.

Complete Specification Published: Sept. 20, 1967.

© Crown Copyright 1967.

Index at acceptance:—G2 C(C4A4, C4B1DY, C4C1, C4C2A, C4C2B2, C4C2X, C4C3AX, C4C3X, C4C5C, C4E1B, C4G2)

Int. Cl.:—G 03 c 1/08

## COMPLETE SPECIFICATION

### Process and Material for the Preparation of Planographic Printing Plates

We, KALLE AKTIENGESellschaft, a Body Corporate organised according to the Laws of Germany, of 190—196 Rheingastrasse, Wiesbaden-Biebrich, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

Copying material for use in the preparation of a planographic printing plate normally consists of a support having a hydrophilic surface, e.g. a support of suitably pretreated aluminium, which carries an adherent positive or negative working light-sensitive coating.

One such copying material, which is described and claimed in Specification No. 950,761, comprises an aluminium support and a coating of a radiation-sensitive substance anchored to the support by an intervening thin layer of a phosphonic acid or a derivative or substitution product thereof.

Planographic printing plates are, however, often prepared by a "do it yourself method", the hydrophilic support and the copying layer (usually as a copying lacquer) being put on the market separately, the final preparation of the copying material by uniting these components being carried out by the user shortly before use.

The present invention is based on our discovery that the copying material described and claimed in Specification No. 950,761 is well suited to the preparation of a planographic printing plate for two reasons. Firstly the thin layer of phosphonic acid, or a derivative or substitution product thereof, on the aluminium support retains its hydrophilic properties notwithstanding long storage under adverse conditions, e.g. of high humidity and temperature

such as are encountered in the tropics. Secondly, in many cases part of said layer is capable of being washed away from the support by water, leaving the remainder of the layer adherent to the support. This is important because it enables dust particles on the surface to be washed off by the consumer prior to application of the light-sensitive coating.

It appears probable that the firmly adhering layer of phosphonic acid which remains on the support after washing is only a few molecules thick. It adheres very firmly to the aluminium by adsorptive and chemical forces. The layer which is capable of being washed off is likewise adsorptively attached but by substantially weaker forces. Altogether a layer having a thickness of about 20 molecules may be initially attached by the adsorptive forces, as has been established analytically by evaluation of adsorption isotherms. It appears likely that the innermost portion having a thickness of about 3 molecules is firmly attached, while the remainder can be washed off with water and phosphonic acid is detectable in the wash water by careful and accurate analysis. Whether any particular phosphonic acid layer contains a portion capable of being washed off can be readily determined by exposing the layer for a time to the action of dust and then washing with water. If the dust is washed off properly, the layer contains a portion which is capable of being washed off.

The invention provides a process for the preparation of a copying material, which comprises subjecting a stored aluminium support, bearing a thin layer of a phosphonic acid or a derivative or substitution product thereof part of which can be removed by washing with water, to treatment with water by washing said layer with water or wiping it with a wet

[Price 4s. 6d.]

sponge or other soft material, and thereafter applying to it a light-sensitive coating.

5 Examples of suitable phosphonic acids and derivatives thereof are substituted or unsubstituted aromatic, cyclic, aliphatic and heterocyclic phosphonic acids, polymers and copolymers of unsaturated phosphonic acids with each other or with other vinyl compounds, as well as derivatives thereof, such as salts or  
10 esters. Especially preferred is polyvinylphosphonic acid.

The copying material may be prepared by immersing a plate or strip of aluminium, if desired after pre-cleaning chemically (e.g. with phosphoric acid) or electrolytically, in a cold  
15 or warm solution of a phosphonic acid or derivative thereof in water or other suitable solvent. The solution may alternatively be applied by means of a roller. After drying, a test is  
20 made to ascertain whether or not the layer contains a portion capable of being washed off.

The material so prepared is cut into sizes to suit the consumer, and then despatched  
25 and stored, or stored first and then despatched, and in some cases then stored again. The light-sensitive coating is then applied by the consumer, after carrying out the washing operation referred to above.

30 The washing should be thorough, in order to remove with certainty any dust and dirt. The firmly adhering layer is not attacked, even in the event of prolonged washing.

35 The light-sensitive coating normally consists of a lacquer containing a light-sensitive substance, a resin acting as a binder, a plasticiser (if desired), a solvent and sometimes also a sensitiser. The following are examples of suitable light-sensitive substances:—

40 Aliphatic and aromatic esters, hydrazides and amides of naphthaquinonediazidesulphonic acids; cinnamalmalonic acid and substitution products and derivatives thereof; diazonium salts of aminodiphenylamine and condensation  
45 products thereof with formaldehyde; ortho- and para-quinonediazides of benzene; anthracene; heterocyclic compounds, for example quinaline, indazole, benzimidazole, fluorene; diphenylene hydroxide; diazo ketones; unsaturated ketones such as those described in  
50 Specification No. 712,991; ortho- and para-iminoquinonediazides; derivatives of alkyl-nitronaphthalenesulphonic acids; nitroaldehydes; acenaphthenes; nitrones; stilbenes; azides and diazides; polymeric diazo compounds and acid condensation products of unsubstituted or substituted diphenylamine-4-  
55 diazonium salts with formaldehyde which may or may not be free from metal salts. Substances which experience a change in electrical conductivity under the action of light, such as are used in electrophotography, e.g. oxadiazoles, imidazoles, triazoles and oxazoles, may  
60 also be used.

65 The process yields, even under tropical

conditions, unobjectionable planographic printing plates with excellent water-acceptance in the non-printing areas.

A further advantage is that practically all known positive and negative working light-sensitive coatings adhere to the phosphonic acid surface and permit long printing runs.

#### EXAMPLE 1:

A mechanically roughened aluminium plate is immersed in a 5% aqueous solution of polyvinylphosphonic acid at 25°C and dried with warm air. The phosphonic acid layer on the plate was found to contain a portion capable of being washed off with water. The coated aluminium plate can be stored, even under  
75 80 tropical conditions, without impairment of its hydrophilic properties.

In order to prepare a light-sensitive, negative-working copying material suitable for the preparation of a planographic printing plate the pretreated aluminium plate, after an appreciable period of storage, is washed with a water spray and the moist plate is coated with a 1% aqueous solution of a crude condensate from paraformaldehyde and diphenylamine - 4 - diazonium chloride by wiping over with a pad of cotton wool. After drying, the copying material is ready for use.

The copying material is exposed to light under a photographic negative and wiped over with a sponge moistened with water to remove the light-sensitive coating from the unexposed areas. The plate is then wiped over with greasy ink. The portions of the coating hardened by light in the exposed areas accept the ink, which is repelled by the extremely hydrophilic phosphonic acid layer in the non-image areas. The image areas can be reinforced in the conventional manner with lacquer.

The printing plate, after development and inking up and lacquering, yields long printing runs.

#### EXAMPLE 2:

A thin aluminium strip is drawn through a bath which contains a solution, at 80°C, of 5% vinylphosphonic acid and 0.1% carboxymethylcellulose in water, and dried. The phosphonic acid layer was found to contain a portion capable of being washed off with water.

The aluminium strip so treated can be despatched and stored without reduction of the hydrophilic properties of its surface. When required, it is cut into sizes, wiped with a moist sponge and then coated, using a pad of cotton wool, with a light-sensitive solution which contains 2 g of 4' - [naphthoquinone - (1,2) - diazide - (2) - sulphonylhydroxy - (5)] - 2',3' - dihydroxybenzophenone, 4 g of a phenol-formaldehyde Novolak and 0.1 g of diethylaminobenzene in butyl acetate.

To prepare a printing plate, the copying material is exposed under a diapositive,

whereby a high-contrast image of the original is formed, and developed by treatment with a 5% aqueous sodium triphosphate solution. When wiped over with greasy ink, the coating accepts the ink in the image areas, while the hydrophilic phosphonic acid layer bared by the developing treatment repels the ink in the non-image areas.

## EXAMPLE 3:

10 An aluminium plate is coated on a whirl-coater with a solution of 2% of a copolymer of styrene and vinylphosphonic acid and 2% of polyvinylphosphonic acid in 10% of water and 86% of methylglycol, and dried. The phosphonic acid layer adheres firmly and contains a portion which can be washed off with water. The plate can be stored for any desired length of time.

20 To prepare a copying material, the aluminium plate is washed with water and then coated, using a pad of cotton wool, with a 1.5% solution in methyl glycol of 1 - [(4' - methylbenzene - 1' - sulphonyl) - imino] - 2 - (2'',5'' - dimethylphenylaminosulphonyl) - benzoquinone - (1,4) - diazide - (4). The material is then dried. To prepare a printing plate, the material is exposed under a negative and developed by treatment with a 0.5% aqueous solution of trisodium phosphate. 30 The plate is then washed with water and inked up.

## EXAMPLE 4:

35 The procedure of Example 3 is followed, using instead of the diazo compound named in Example 3 the same amount of benzoquinone - (1,4) - diazide - (4) - 2(N -  $\beta$  - naphthyl) - sulphonamide.

## EXAMPLE 5:

40 An aluminium plate is immersed for 5 minutes at 90°C in a 10% aqueous-ammoniacal solution of 3-aminophenylphosphonic acid, then dried and stored. The phosphonic acid layer contains a portion capable of being washed off.

45 To prepare a copying material, the support is washed and coated by hand with a 2% solution of the ester from naphthaquinone - (1,2) - diazide - (2) - sulphonic acid chloride-

(4) and 1 - methyl - 2 - (2' - hydroxyphenyl) - benzimidazole and then dried. After exposure under a negative, development with 2% aqueous phosphoric acid and inking up, a printing plate for medium printing runs is obtained. 50

## EXAMPLE 6:

55 The procedure of Example 5 is followed using, instead of the diazo compound named therein, the naphthoquinone - (1,2) - diazide - (2) - 4 - sulphonic acid ester of 7 - hydroxy - 2 - methyl - N - (ethyl) - naphtho - 1',2': 4,5-imidazole. 60

## EXAMPLE 7:

Aluminium is treated with phosphonic acid as stated in Example 1, washed with water, stored, and sensitised when required with a 2% solution in ethyl glycol of 4' - [naphthoquinone - (1,2) - diazide - (2) - sulphonyl - hydroxy - (5)] - 1' - iso - octylbenzene. After exposure under a diapositive and development with 5% aqueous solution of trisodium phosphate, and inking up, a good printing plate is obtained. 65 70

## WHAT WE CLAIM IS:—

1. A process for the preparation of a copying material, which comprises subjecting a stored aluminium support, bearing a thin layer of a phosphonic acid or a derivative or substitution product thereof part of which can be removed by washing with water, to treatment with water by washing said layer with water or wiping it with a wet sponge or other soft material, and thereafter applying to it a light-sensitive coating. 75 80

2. A process as claimed in claim 1, substantially as described herein with reference to any of the foregoing Examples. 85

3. A copying material when produced by the process claimed in any of the preceding claims.

4. A planographic printing plate when produced from a copying material as claimed in claim 3. 90

BREWER & SON,  
Chartered Patent Agents,  
5—9 Quality Court,  
Chancery Lane,  
London, W.C.2.